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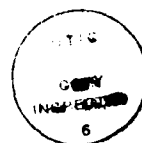


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<p>A series of compounds of the type <math>R_2MCH_2PPh_2</math> (<math>R = CH_2CMe_3</math>, <math>CH_2SiMe_3</math>; <math>M = Ga, In</math>) have been prepared by metathetical reactions between the appropriate diorganometal halide and <math>LiCH_2PPh_2</math> in pentane or <math>Et_2O</math> at <math>-78^\circ C</math>. All compounds were characterized by physical properties, partial elemental analyses (C, H), cryoscopic molecular weight measurements in benzene solution as well as IR, <math>^1H</math> NMR and <math>^{31}P</math> NMR spectroscopic data. All appropriate data support the existence of dimeric molecules. The monomeric species dimerize by apparent Lewis acid-base interactions. These interactions are sufficiently strong that the compounds do not form stable adducts with oxygen- or nitrogen-containing Lewis bases.</p> <p style="text-align: right;">(continued)</p>					
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$[(\text{Me}_3\text{CCH}_2)_2\text{InCH}_2\text{PPh}_2]_2 \cdot \text{C}_6\text{D}_6$  crystallizes in the centrosymmetric triclinic space group  $P\bar{1}$  (No. 2) with  $a = 13.142(3)$ ,  $b = 15.109(3)$ ,  $c = 15.746(4)\text{\AA}$ ,  $\alpha = 85.27(2)$ ,  $\beta = 67.99(2)$ ,  $\gamma = 66.00(1)^\circ$ ,  $V = 2639(1)\text{\AA}^3$  and  $Z = 2$ . Diffraction data (Mo K $\alpha$ ,  $2\theta = 4.5$ - $45.0^\circ$ ) were collected on a Syntex P2<sub>1</sub> diffractometer; the structure was solved and refined to  $R_F = 6.0\%$  and  $R_{wF} = 6.4\%$  for all 6932 independent reflections ( $R_F = 4.5\%$  and  $R_{wF} = 6.2\%$  for those 5495 data with  $F_o \geq 6(F_\sigma)$ ). The crystal is composed of two crystallographically independent  $[(\text{Me}_3\text{CCH}_2)_2\text{InCH}_2\text{PPh}_2]_2$  molecules (each having precise  $C_i$  symmetry) and a  $\text{C}_6\text{D}_6$  molecule of solvation. The two independent  $[(\text{Me}_3\text{CCH}_2)_2\text{InCH}_2\text{PPh}_2]_2$  molecules have similar configurations. Each is based upon a six-membered  $\text{In-CH}_2\text{-P-In-CH}_2\text{-P}$  ring with a chair conformation. Bond lengths of interest include:  $\text{In-P} = 2.694(2)$ - $2.703(2)\text{\AA}$ ,  $\text{In-CH}_2 = 2.255(7)$ - $2.261(8)\text{\AA}$  and  $\text{In-(neopentyl)} = 2.216(7)$ - $2.234(7)\text{\AA}$ .



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Methylene Bridged Group 13-15 Compounds,  $R_2MCH_2PPh_2$  ( $R = CH_2CMe_3$ ,  $CH_2SiMe_3$ ;  $M = Ga, In$ ). Crystal Structure of  $[(Me_3CCH_2)_2InCH_2PPh_2]_2 \cdot C_6D_6$ , a Molecule Containing an In-C-P-In-C-P Ring in a Chair Conformation

by

O. T. Beachley, Jr., Michael A. Banks, Melvyn Rowen Churchill,

William G. Feighery and James C. Fettingner

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Methylene Bridged Group 13-15 Compounds,  $R_2MCH_2PPh_2$  ( $R = CH_2CMe_3$ ,  $CH_2SiMe_3$ ;  $M = Ga, In$ ). Crystal Structure of  $[(Me_3CCH_2)_2InCH_2PPh_2]_2 \cdot C_6D_6$ , a Molecule Containing an In-C-P-In-C-P Ring in a Chair Conformation

by

O. T. Beachley, Jr.,\* Michael A. Banks, Melvyn Rowen Churchill,\*  
William G. Feighery and James C. Fettingner

Abstract

A series of compounds of the type  $R_2MCH_2PPh_2$  ( $R = CH_2CMe_3$ ,  $CH_2SiMe_3$ ;  $M = Ga, In$ ) have been prepared by metathetical reactions between the appropriate diorganometal halide and  $LiCH_2PPh_2$  in pentane or  $Et_2O$  at  $-78^\circ C$ . All compounds were characterized by physical properties, partial elemental analyses (C, H), cryoscopic molecular weight measurements in benzene solution as well as IR,  $^1H$  NMR and  $^{31}P$  NMR spectroscopic data. All appropriate data support the existence of dimeric molecules. The monomeric species dimerize by apparent Lewis acid-base interactions. These interactions are sufficiently strong that the compounds do not form stable adducts with oxygen- or nitrogen-containing Lewis bases.

$[(Me_3CCH_2)_2InCH_2PPh_2]_2 \cdot C_6D_6$  crystallizes in the centrosymmetric triclinic space group  $P\bar{1}$  (No. 2) with  $a = 13.142(3)$ ,  $b = 15.109(3)$ ,  $c = 15.746(4) \text{ \AA}$ ,  $\alpha = 85.27(2)$ ,  $\beta = 67.99(2)$ ,  $\gamma = 66.00(1)^\circ$ ,  $V = 2639(1) \text{ \AA}^3$  and  $Z =$

2. Diffraction data (Mo K $\alpha$ ,  $2\theta = 4.5-45.0^\circ$ ) were collected on a Syntex P2<sub>1</sub> diffractometer; the structure was solved and refined to  $R_F = 6.0\%$  and  $R_{wF} = 6.4\%$  for all 6932 independent reflections ( $R_F = 4.5\%$  and  $R_{wF} = 6.2\%$  for those 5495 data with  $|F_o| > 6\sigma(|F_o|)$ ). The crystal is composed of two crystallographically independent  $[(Me_3CCH_2)InCH_2PPh_2]_2$  molecules (each having precise  $C_1$  symmetry) and a  $C_6D_6$  molecule of solvation. The two independent  $[(Me_3CCH_2)InCH_2PPh_2]_2$  molecules have similar configurations. Each is based upon a six-membered In-CH<sub>2</sub>-P-In-CH<sub>2</sub>-P ring with a chair conformation. Bond lengths of interest include: In-P = 2.694(2)-2.703(2)Å, In-CH<sub>2</sub> = 2.255(7)-2.261(8)Å and In-(neopentyl) = 2.216(7)-2.234(7)Å.

### Introduction

Single source precursors of the types  $R_3MER'_3$ <sup>1</sup> and  $R_2MER'_2$ <sup>2</sup> (M = group 13 element, E = group 15 element) have been used to prepare group 13-15 materials such as GaAs and InP. An alternative class of potential precursors which contain only the group 13 and 15 elements, carbon and hydrogen are compounds of the type  $R_2MCH_2ER'_2$ . This class of compounds has a methylene group which bridges the group 13 and 15 elements in order to establish as well as to fix the group 13/15 ratio at one as required for the desired material. Thus, compounds of this type incorporate simple Lewis acid and base sites without the possibility of pi bonding in the monomeric species between the vacant orbital on the group 13 element and the electron pair on the group 15 element. The only reported heavier 13-CH<sub>2</sub>-15 species are aluminum compounds including  $Cl_{3-x}Al(CH_2PMe_2)_x$ ,<sup>3</sup>  $Me_{3-x}Al(CH_2PMe_2)_x$  (x = 1-3)<sup>3,4,5</sup> and  $LiAl(CH_2PMe_2)_4$ .<sup>5</sup>

In this paper we report the synthesis and characterization of  $R_2MCH_2PPh_2$  (R = CH<sub>2</sub>CMe<sub>3</sub>, CH<sub>2</sub>SiMe<sub>3</sub>; M = Ga, In). All compounds were characterized by elemental analyses (C, H), physical properties, cryoscopic molecular weight studies in benzene as well as IR, <sup>1</sup>H NMR and <sup>31</sup>P NMR spectral data. In addition, an X-ray structural study was used to investigate the crystalline state of  $(Me_3CCH_2)_2InCH_2PPh_2$ .

### Experimental

All compounds described in this investigation were extremely sensitive to oxygen and moisture and were manipulated in a standard vacuum line or under a purified argon atmosphere. The compounds  $\text{Ga}(\text{CH}_2\text{CMe}_3)_2\text{Cl}$ ,<sup>6</sup>  $\text{In}(\text{CH}_2\text{CMe}_3)_2\text{Cl}$ ,<sup>7</sup>  $\text{Ga}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$ ,<sup>6</sup>  $\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$ ,<sup>8</sup>  $\text{LiCH}_2\text{PPh}_2$ <sup>9</sup> and  $\text{Li}(\text{TMEDA})\text{CH}_2\text{PPh}_2$ <sup>10</sup> were prepared and purified by literature methods. Solvents were dried by conventional procedures. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Infrared spectra of Nujol mulls between CsI plates were recorded by means of a Perkin-Elmer 683 spectrometer. Absorption intensities are reported with the abbreviations vs(very strong), s(strong), m(medium), w(weak), vw(very weak) and sh(shoulder). The  $^1\text{H}$  NMR spectra were recorded at 90 MHz by using a Varian Model EM-390 spectrometer. Chemical shifts are reported in  $\delta$  units (ppm) and are referenced to  $\text{SiMe}_4$  as  $\delta$  0.00 and benzene as  $\delta$  7.13. The  $^{31}\text{P}$  NMR spectra were recorded at 36.23 MHz by using a JEOL FX-90Q spectrometer. The proton decoupled spectra are reported relative to 85%  $\text{H}_3\text{PO}_4$  as  $\delta = 0.00$  ppm. All samples for NMR spectra were contained in sealed NMR tubes. Melting points were observed in sealed capillaries. Molecular weights were measured cryoscopically in benzene by using an instrument similar to that described by Shriver and Drezdson.<sup>11</sup>

Synthesis of  $(\text{Me}_3\text{CCH}_2)_2\text{GaCH}_2\text{PPh}_2$ . A 100-mL round-bottom two-neck flask was charged with 1.467 g (5.929 mmol) of  $\text{Ga}(\text{CH}_2\text{CMe}_3)_2\text{Cl}$  and fitted with a side-arm dumper containing 1.188 g (5.968 mmol) of  $\text{LiCH}_2\text{PPh}_2$ . After the organogallium reagent was dissolved in 40 mL of pentane and cooled to  $-78^\circ\text{C}$ ,  $\text{LiCH}_2\text{PPh}_2$  was slowly added to the mixture with stirring for 15 minutes. The mixture was allowed to warm to ambient temperature on its own accord and stirred for 18 h. The colorless solid remaining after the pentane was

removed was extracted six times with a benzene/pentane mixture (45 mL/20 mL) and finally recrystallized from benzene to give 1.910 g (4.644 mmol) of  $(\text{Me}_3\text{CCH}_2)_2\text{GaCH}_2\text{PPh}_2$  in 87.6% yield based on  $\text{Ga}(\text{CH}_2\text{CMe}_3)_2\text{Cl}$ .

$(\text{Me}_3\text{CCH}_2)_2\text{GaCH}_2\text{PPh}_2$ . mp: crystals became opaque with rounded edges at 178-183 °C and then melted at 187-188°C.  $^1\text{H}$  NMR ( $\text{C}_6\text{H}_6$ ,  $\delta$ ): 0.62 (d,  $^3\text{J}_{\text{PGaCH}} = 3.6$  Hz, 4 H,  $-\text{CH}_2\text{Ga}-$ ), 1.03 (s, 18 H,  $-\text{CMe}_3$ ), 1.63 (dd,  $^2\text{J}_{\text{PCH}} = 11.7$  Hz,  $^3\text{J}_{\text{PGaCH}} = 8.1$  Hz, 2 H,  $-\text{CH}_2\text{P}-$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): -10.1 (s).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{d}^8\text{-THF}$ ,  $\delta$ ) -9.96 (s).  $[(\text{Me}_3\text{CCH}_2)_2\text{GaCH}_2\text{PPh}_2] \cdot 0.75 \text{ C}_6\text{H}_6$  Anal. Calcd.: C, 70.29; H, 8.28. Found: C, 70.23; H, 8.58. (The compound  $(\text{Me}_3\text{CCH}_2)_2\text{GaCH}_2\text{PPh}_2$  was crystallized from benzene solution.) IR (Nujol mull,  $\text{cm}^{-1}$ ): 3085 (vw), 3070 (vw), 3050 (vw), 3018 (vw), 1809 (vw, br), 1585 (vw), 1570 (vw), 1355 (m), 1305 (vw), 1224 (vw), 1182 (vw), 1155 (vw), 1135 (vw), 1095 (w), 1070 (w), 1024 (w), 995 (w), 785 (w), 772 (w), 745 (m), 738 (s), 718 (sh), 710 (m), 701 (sh), 693 (s), 640 (w), 620 (w), 560 (w), 534 (w), 505 (w), 474 (w).

Synthesis of  $(\text{Me}_3\text{CCH}_2)_2\text{InCH}_2\text{PPh}_2$ . The compound  $(\text{Me}_3\text{CCH}_2)_2\text{InCH}_2\text{PPh}_2$  (1.291 g, 2.828 mmol, 92.3% yield) was prepared from 0.897 g (3.07 mmol) of  $\text{In}(\text{CH}_2\text{CMe}_3)_2\text{Cl}$  and 0.635 g (3.08 mmol)  $\text{LiCH}_2\text{PPh}_2$  in pentane by using the procedure previously described. Crystals of  $(\text{Me}_3\text{CCH}_2)_2\text{InCH}_2\text{PPh}_2$  suitable for an X-ray structural study were obtained from a saturated  $\text{d}_6$ -benzene solution at ambient temperature.

$(\text{Me}_3\text{CCH}_2)_2\text{InCH}_2\text{PPh}_2$ . mp: 205.5-209.5 °C.  $^1\text{H}$  NMR ( $\text{C}_6\text{H}_6$ ,  $\delta$ ): 0.70 (d,  $^3\text{J}_{\text{PInCH}} = 8.6$  Hz, 4 H,  $-\text{CH}_2\text{In}-$ ), 0.90 (s, 18 H,  $-\text{CMe}_3$ ), 1.46 (dd,  $^2\text{J}_{\text{PCH}} = 9.9$  Hz,  $^3\text{J}_{\text{PInCH}} = 4.5$  Hz, 2 H,  $-\text{CH}_2\text{P}-$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): -8.41 (s). Cryoscopic molecular weight, formula weight 456.47 (calculated molality, observed molality, association): 0.0640, 0.0327, 1.96. Anal. Calcd.: C, 60.52; H, 7.51. Found: C, 60.58; H, 7.68. IR (Nujol mull,  $\text{cm}^{-1}$ ): 3080



(vw), 3058 (vw), 1870 (vw), 1803 (vw), 1581 (vw), 1569 (vw), 1478 (sh, m), 1431 (vs), 1355 (s), 1330 (w), 1324 (w), 1299 (w), 1275 (w), 1230 (m), 1210 (w), 1180 (vw), 1165 (vw), 1110 (w), 1094 (w), 1085 (vw, sh), 1065 (vw), 1022 (vw), 1008 (w), 995 (w), 988 (w), 962 (vw), 945 (m), 910 (vw), 838 (vw), 768 (m), 740 (m), 732 (s), 717 (m), 699 (m, sh), 689 (vs), 674 (m), 668 (m), 608 (m), 561 (w), 516 (m), 488 (vw), 460 (vw), 445 (vw), 338 (vw).

Synthesis of  $(\text{Me}_3\text{SiCH}_2)_2\text{GaCH}_2\text{PPh}_2$ . The compound  $(\text{Me}_3\text{SiCH}_2)_2\text{GaCH}_2\text{PPh}_2$  (2.118 g, 4.778 mmol, 94.5% yield based on  $\text{Ga}(\text{CH}_2\text{CMe}_3)_2\text{Cl}$ ) was prepared from 1.413 g (5.052 mmol) of  $\text{Ga}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$  and  $\text{LiCH}_2\text{PPh}_2$  (1.058 g, 5.133 mmol) by using the procedure previously described. Crystals were obtained from a saturated benzene solution at ambient temperature.

$(\text{Me}_3\text{SiCH}_2)_2\text{GaCH}_2\text{PPh}_2$ . mp: crystals appeared glassy at 180 °C and melted at 207-212 °C.  $^1\text{H}$  NMR ( $\text{C}_6\text{H}_6$ ,  $\delta$ ): -0.61 (d,  $^3J_{\text{PGaCH}} = 4.2$  Hz, 4 H,  $-\text{CH}_2\text{Ga}-$ ), 0.11 (s, 18 H,  $-\text{SiMe}_3$ ), 1.62 (dd,  $^2J_{\text{PCH}} = 10.8$  Hz,  $^3J_{\text{PGaCH}} = 7.2$  Hz, 2 H,  $-\text{CH}_2\text{P}-$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 0.21 M,  $\delta$ ): -0.16 (dd,  $^2J_{\text{PCGaC}} = 7.4$  Hz,  $^3J_{\text{PGaC}} = 3.7$  Hz,  $-\text{CH}_2\text{P}-$ ), 3.31 (s,  $-\text{SiMe}_3$ ), 7.48 (dd,  $J_{\text{PC}} = 18.3$  Hz,  $^2J_{\text{PGaC}} = 6.1$  Hz,  $-\text{CH}_2\text{P}-$ ).  $^{29}\text{Si}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): 17.7 (s).  $^{31}\text{P}\{^1\text{H}\}$  ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): -10.2 (s). Anal. Calcd.: C, 56.88; H, 7.73; P, 6.99. Found: C, 57.02; H, 7.62; P, 6.50. Cryoscopic molecular weight, formula weight 443.37 (calculated molality, observed molality, association): 0.136, 0.0691, 1.98; 0.0911, 0.0452, 2.02; 0.0631, 0.0326, 1.94. IR (Nujol mull,  $\text{cm}^{-1}$ ): 3080 (w), 3060 (w), 1735 (vw, br), 1586 (w), 1570 (w), 1330 (w), 1303 (w), 1255 (s), 1240 (s), 1185 (w), 1097 (m), 1070 (w), 1028 (m), 1005 (s), 998 (s), 978 (s), 967 (m), 910 (w), 853 (s), 821 (s), 770 (m), 750 (m, sh), 737 (s), 723 (s), 703 (m), 692 (s), 678 (m), 635 (s), 612 (w), 588 (w), 552 (s), 520 (m), 510 (m), 495 (w), 474 (m), 430 (w), 347 (w).

Synthesis of  $(\text{Me}_3\text{SiCH}_2)_2\text{InCH}_2\text{PPh}_2$ . The compound  $(\text{Me}_3\text{SiCH}_2)_2\text{InCH}_2\text{PPh}_2$  was synthesized from  $\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$  and  $\text{LiCH}_2\text{PPh}_2$  or  $\text{Li}(\text{TMEDA})\text{CH}_2\text{PPh}_2$  in pentane or diethyl ether, respectively, by using the procedure previously described. The product was isolated in 92.4% yield when  $\text{LiCH}_2\text{PPh}_2/\text{C}_5\text{H}_{12}$  were used, whereas only a 79.4% yield was obtained from  $\text{Li}(\text{TMEDA})\text{CH}_2\text{PPh}_2/\text{OEt}_2$ . Crystals were grown after slow diffusion of anhydrous pentane into a benzene solution of the compound. All properties of the two products were identical.

$(\text{Me}_3\text{SiCH}_2)_2\text{InCH}_2\text{PPh}_2$ . mp: 208-210 °C.  $^1\text{H}$  NMR ( $\text{C}_6\text{H}_6$ ,  $\delta$ ): -0.57 (d,  $^3\text{J}_{\text{PInCH}} = 3.6$  Hz, 4 H,  $-\text{CH}_2\text{In}-$ ), 0.14 (s, 18 H,  $-\text{SiMe}_3$ ), 1.50 (dd,  $^2\text{J}_{\text{PCH}} = 10.8$  Hz,  $^3\text{J}_{\text{PInCH}} = 4.5$  Hz, 2 H,  $-\text{CH}_2\text{P}-$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): -10.0 (s). Cryoscopic molecular weight, formula weight 488.47 (calculated molality, observed molality, association): 0.127, 0.0726, 1.75; 0.114, 0.0679, 1.67; 0.0735, 0.0414, 1.78; 0.0938, 0.0564, 1.66; 0.0600, 0.0347, 1.75. Anal. Calcd.: C, 51.64; H, 7.22. Found: C, 51.71; H, 7.27. IR (Nujol mull,  $\text{cm}^{-1}$ ): 3070 (w), 3060 (w), 3050 (w), 1802 (vw), 1582 (vw), 1570 (vw), 1478 (m), 1431 (s), 1350 (w), 1324 (w), 1298 (w), 1252 (w, sh), 1238 (s), 1159 (vw), 1152 (vw), 1110 (vw), 1100 (vw), 1095 (w, sh), 1085 (w), 1065 (w), 1023 (w), 995 (w), 990 (vw), 965 (m, sh), 960 (m), 952 (m), 940 (m), 928 (m), 912 (w, sh), 854 (s), 838 (m), 820 (vs), 769 (m), 748 (m, sh), 742 (vs), 732 (vs), 720 (s), 700 (m), 688 (vs), 678 (m, sh), 616 (m), 562 (w), 550 (w), 518 (m), 490 (m), 482 (m), 462 (m), 390 (vw), 338 (vw).

Lewis Acid-Base Studies of  $\text{R}_2\text{MCH}_2\text{PPh}_2$  Compounds ( $\text{R} = \text{CH}_2\text{CMe}_3$  or  $\text{CH}_2\text{SiMe}_3$ ;  $\text{M} = \text{Ga}$  or  $\text{In}$ ). Proton NMR spectroscopy was used to investigate the Lewis acidity of  $\text{R}_2\text{MCH}_2\text{PPh}_2$ . A reaction tube equipped with an NMR tube as a side-arm was charged with a weighed amount of the desired compound. The tube was fitted with an adapter and evacuated. The appropriate base (in

excess) was distilled into the tube. The mixture was allowed to stir 15-18 h at ambient temperature. The base was removed by vacuum distillation and the solid remaining in the tube was evacuated for 15 hours. Five mL of benzene was distilled into the reaction tube and an aliquot (ca. 0.7 mL) of the resulting solution was decanted into the NMR tube. The mixture in the NMR tube was frozen at  $-196^{\circ}\text{C}$  and the tube was then flame-sealed.

No stable room temperature Lewis acid-Lewis base adducts,  $(\text{Me}_3\text{SiCH}_2)_2\text{GaCH}_2\text{PPh}_2 \cdot \text{L}$ , were observed for  $\text{L} = \text{Et}_2\text{O}$ , THF, DME (dimethoxyethane), MeCH,  $\text{NMe}_3$  and TMEDA. Similar studies with  $(\text{Me}_3\text{YCH}_2)_2\text{MCH}_2\text{PPh}_2$ , where  $\text{Y} = \text{Si}$  or  $\text{C}$ ;  $\text{M} = \text{Ga}$  or  $\text{In}$ , revealed no adducts for  $\text{L} = \text{Et}_2\text{O}$ , THF and TMEDA.

The compound  $(\text{Me}_3\text{SiCH}_2)_2\text{GaCH}_2\text{PPh}_2$  does form an apparent adduct with excess  $\text{NMe}_3$  in benzene solution. A sample of the compound was reacted with a four-fold excess of  $\text{NMe}_3$  in protic benzene and poured into an NMR tube.  $^1\text{H}$  NMR ( $\text{C}_6\text{H}_6$ ,  $\delta$ ):  $-0.81$  (s, 1 H,  $-\text{CH}_2-$ ),  $0.14$  (s, 6 H,  $-\text{SiMe}_3/-\text{CH}_2-$ ),  $2.05$  (s,  $\text{NMe}_3$ ).

Collection of X-Ray Diffraction Data for  $[(\text{Me}_3\text{CCH}_2)_2\text{InCH}_2\text{PPh}_2]_2 \cdot \text{C}_6\text{D}_6$ .  
A colorless crystal of approximate orthogonal dimensions  $0.3 \times 0.3 \times 0.4$  mm, and rather "cube-like" in shape, was mounted in a thin-walled glass capillary under a carefully purified argon atmosphere. The crystal was aligned and centered on a Syntex P2<sub>1</sub> automated four-circle diffractometer. Determination of accurate cell dimensions, the orientation matrix and Laue symmetry were carried out as described previously.<sup>12</sup> Details of this and of data collection are provided in Table 1.

A survey of the data set revealed no systematic absences and no symmetry other than the Friedel condition. The crystal thus belongs to the triclinic class, possible space groups being the centrosymmetric  $\text{P}\bar{1}$  ( $\text{C}_i^1$ ; No.

2) or the noncentrosymmetric  $P1$  ( $C_1^1$ ; No. 2). The former, centrosymmetric, alternative was adjudged the most probable based upon cell content and intensity statistics; this was confirmed by the successful solution of the structure in the higher symmetry space group.

All data were corrected for the effects of absorption and symmetry equivalent reflections were averaged; the resulting unique data were corrected for Lorentz and polarization effects, were converted to unscaled  $|F_o|$  values and were placed on an approximately absolute scale by means of a Wilson plot. Any reflection with  $I(\text{net}) < 0$  was assigned the value  $|F_o| = 0$  and was retained in the data set.

#### Solution and Refinement of the Structure of

$[(\text{Me}_3\text{CCH}_2)_2\text{InCH}_2\text{PPh}_2]_2 \cdot \text{C}_6\text{H}_6$ . All calculations were performed on our locally modified set of Syntex XTL computer programs. The calculated structure factors were based on the analytical form of the scattering factors for neutral atoms;<sup>13a</sup> both the real ( $\Delta f'$ ) and imaginary ( $i\Delta f''$ ) components of anomalous dispersion<sup>13b</sup> were included for all atoms. The function minimized during full-matrix least squares refinement was  $\sum w(|F_o| - |F_c|)^2$  where  $w^{-1} = \{[\sigma(|F_o|)]^2 + [0.015|F_o|]^2\}$ .

The positions of the indium atoms ( $Z = 49$ ) were determined from a Patterson map. There are two independent indium atoms in the asymmetric unit. In(1) and In(1)\* define the core of a dimeric molecule centered about the inversion center at  $1/2, 1/2, 1/2$  while In(2) and In(2)\* define the core of a second molecule centered about  $1/2, 0, 0$ . A difference-Fourier synthesis ( $R_F = 40.6\%$ )<sup>14</sup> revealed the positions of the two independent phosphorus atoms and 37 of the carbon atoms. All remaining carbon atoms (including six from a molecule of solvation,  $\text{C}_6\text{D}_6$ , lying in a general position) were located from a second difference-Fourier synthesis.

Refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms led to convergence with  $R_F = 6.0\%$ ,  $R_{wF} = 6.4\%$  and  $GOF = 2.42$  for 505 variables refined against all 6932 independent reflections.

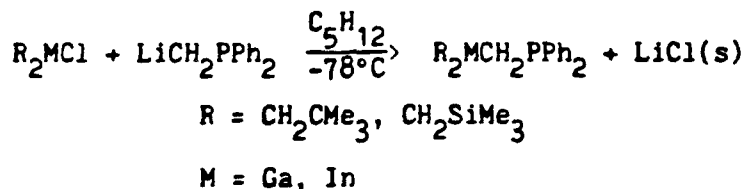
Discrepancy indices for those 6021 data with  $|F_o| > 3\sigma(|F_o|)$  were  $R_F = 5.0\%$  and  $R_{wF} = 6.3\%$ ; for those 5495 data with  $|F_o| > 6\sigma(|F_o|)$  these were further reduced to  $R_F = 4.5\%$  and  $R_{wF} = 6.2\%$ .

Contributions from all hydrogen atoms except for those on methyl groups of the neopentyl ligands were included in calculated positions with  $d(C-H) = 0.95 \text{ \AA}$ .<sup>15</sup> (Methyl hydrogens were omitted because of limited computer memory.)

A final difference-Fourier synthesis showed no unexpected features and an analysis of  $\Sigma w(|F_o| - |F_c|)^2$  as a function of Miller indices,  $|F_o|$ ,  $(\sin \theta)/\lambda$  and sequence number showed no unusual trends. The structure is thus correct and complete and the weighting scheme satisfactory. Final atomic coordinates are collected in Table 2.

### Results and Discussion

A series of compounds of the general type  $R_2MCH_2PPh_2$  ( $R = CH_2CMe_3$ ,  $CH_2SiMe_3$ ;  $M = Ga, In$ ) have been prepared and have been fully characterized. The characterization data include partial elemental analyses (C, H), physical properties, cryoscopic molecular weight measurements in benzene solution as well as IR,  $^1H$  NMR and  $^{31}P$  NMR spectroscopic data. In addition, a single crystal X-ray structural study was used to define the nature of  $(Me_3CCH_2)_2InCH_2PPh_2$  in the solid state. All compounds were prepared in high yield, typically greater than 90%, by using a metathetical reaction as summarized by the following equation. When the reagents were combined in the presence of pentane at  $-78^\circ C$  and then the reaction mixture was warmed



to room temperature, high yields of products were obtained. If the reagents were mixed at room temperature, low yields of products which were gray in color were observed. The gray color suggests decomposition of the organometallic species.

Crystals of bis(neopentyl)[(diphenylphosphino)methyl]indium(III) are composed to two independent molecules of composition  $[(Me_3CCH_2)_2InCH_2PPh_2]_2$  (each of which lies on a crystallographic inversion center - molecule 1 about  $1/2, 1/2, 1/2$  and molecule 2 about  $1/2, 0, 0$ ) and a  $C_6D_6$  molecule of solvation in a general position. The molecular units are separated by normal van der Waals' distances; there are no abnormally short intermolecular contacts. Distances and angles are provided in Tables 3 and

4. The two independent  $[(\text{Me}_3\text{CCH}_2)_2\text{InCH}_2\text{PPh}_2]_2$  molecules have similar configurations. The labeling for molecule 1 is shown in Figure 1.

Subsequent discussion will focus on dimensions in molecule 1, with equivalent dimensions for molecule 2 given in square brackets. Equivalent values for the two molecules appear side-by-side in Tables 3 and 4. The system P(1)-In(1)-C(1)-P(1')-In(1')-C(1') [P(2)-In(2)-C(2)-P(2')-In(2')-C(2')] defines a six-membered ring with a "chair" conformation; the In-P...In'-P' moiety is planar with C(1) and C(1') [C(2) and C(2')] lying above and below this plane, respectively. (The possible "boat" conformation is disfavored since it would lead to substantial interaction between  $\text{CH}_2\text{CMe}_3$  groups on indium and Ph groups on phosphorus (see Figure 1)).

Indium-neopentyl bond lengths are In(1)-C(11) = 2.226(8)Å and In(1)-C(21) = 2.216(7)Å [In(2)-C(51) = 2.234 (7)Å and In(2)-C(61) = 2.211(10)Å], the average being In-C(neopentyl) = 2.222Å. These distances are comparable to those observed in  $[(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2]_3$ <sup>16</sup> of 2.182(6)Å and 2.210(7)Å (average 2.196Å). The intraring In- $\text{CH}_2$  distance is slightly longer with In(1)-C(1) = 2.261(8)Å [In(2)-C(2) = 2.255(7)Å], the average value being 2.258Å.

The indium-phosphorus distances are In(1)-P(1) = 2.694(2)Å [In(2)-P(2) = 2.703(2)Å], average 2.695Å. The difference between the average In-P and In- $\text{CH}_2$  (ring) distances is 0.437Å. Since this is somewhat larger than the difference in covalent radii between P and C(sp<sup>3</sup>) (i.e., 1.10Å - 0.772Å = 0.33Å),<sup>17</sup> it appears that the In-P bonds are relatively weak. The In-P distances can be compared to those in  $[(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2]_3$ <sup>16</sup> of 2.677(2)Å and 2.699(2)Å. However, since all In-P bonds in  $[(\text{Me}_3\text{CCH}_2)_2\text{InCH}_2\text{PPh}_2]_2$  can be viewed as donor-acceptor bonds, it might be more appropriate to compare the In-P distance to those in simple adducts such as

$\text{Me}_3\text{In}\cdot\text{P}(\text{Ph}_2)\text{CH}_2\text{CH}_2(\text{Ph}_2)\text{P}\cdot\text{InMe}_3$ <sup>18</sup> of 2.755(4)Å,  $\text{Cl}_3\text{In}\cdot 2\text{PPh}_3$ <sup>19</sup> of 2.723(5) and 2.701(5)Å and  $\text{Me}_3\text{In}\cdot\text{PMe}_3$ <sup>18</sup> of 2.683(4)Å.

The intraring P-C distances are  $\text{P}(1)-\text{C}(1') = \text{P}(1') = \text{C}(1) = 1.809(7)\text{Å}$  [ $\text{P}(2)-\text{C}(2') = \text{P}(2')-\text{C}(2) = 1.812(7)\text{Å}$ ], with an average value of 1.811Å. These are slightly shorter than the predicted  $\text{P-C}(\text{sp}^3)$  single bond distance of 1.87Å.

The angles about the indium atoms deviate substantially from the ideal tetrahedral value of 109.47°. The largest angle is that between the two bulky neopentyl ligands, with  $\text{C}(11)-\text{In}(1)-\text{C}(21) = 122.13(30)^\circ$  [ $\text{C}(51)-\text{In}(2)-\text{C}(61)] = 123.10(31)^\circ$ ]. The corresponding C-In-C angle in  $[(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2]_3$  is substantially larger at 143.11(26)°. Intermediate values are found for the  $\text{CH}_2-\text{In}-\text{C}(\text{neopentyl})$  angles with  $\text{C}(1)-\text{In}(1)-\text{C}(11) = 113.57(27)^\circ$  and  $\text{C}(1)-\text{In}(1)-\text{C}(21) = 116.81(28)^\circ$  [ $\text{C}(2)-\text{In}(2)-\text{C}(51) = 113.57(26)^\circ$  and  $\text{C}(2)-\text{In}(2)-\text{C}(61) = 115.69(30)^\circ$ ]. The smallest angles are the P-In-C angles with  $\text{P}(1)-\text{In}(1)-\text{C}(1) = 100.76(19)^\circ$ ,  $\text{P}(1)-\text{In}(1)-\text{C}(11) = 102.06(21)^\circ$  and  $\text{P}(1)-\text{In}(1)-\text{C}(21) = 94.85(22)^\circ$  [ $\text{P}(2)-\text{In}(2)-\text{C}(2) = 99.35(18)^\circ$ ,  $\text{P}(2)-\text{In}(2)-\text{C}(51) = 101.94(19)^\circ$  and  $\text{P}(2)-\text{In}(2)-\text{C}(61) = 96.49(24)^\circ$ ].

Angles about phosphorus also show some irregularities, but to a lesser degree than for indium. Here the most notable feature is that the Ph-P-Ph angles are the smallest, with  $\text{C}(31)-\text{P}(1)-\text{C}(41) = 101.48(32)^\circ$  [ $\text{C}(71)-\text{P}(2)-\text{C}(81) = 103.08(32)^\circ$ ];  $\text{CH}_2-\text{P}-\text{Ph}$  angles have intermediate values of 106.92(33)-108.31(31)° [106.58(33)-107.81(32)°]; In-P-C angles are the largest with values of 108.66(23)°-115.92(23)° [109.06(23)°-116.86(35)°].

In-C-C angles involving the α-carbons of the neopentyl groups are all expanded from the ideal tetrahedral value, with  $\text{In}(1)-\text{C}(11)-\text{C}(12) = 120.42(52)^\circ$  and  $\text{In}(1)-\text{C}(21)-\text{C}(22) = 119.35(57)^\circ$  [ $\text{In}(2)-\text{C}(51)-\text{C}(52) = 120.07(48)^\circ$  and  $\text{In}(2)-\text{C}(61)-\text{C}(62) = 122.76(64)^\circ$ ].



Other distances and angles in the  $[(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2\text{CH}_2]_2$  molecules, and in the  $\text{C}_6\text{D}_6$  molecule of solvation (defined by  $\text{C}(91) + \text{C}(96)$ ) all lie within the accepted ranges.

The cryoscopic molecular weight studies for benzene solutions suggest the presence of dimers for the compounds in solution as was identified for the solid,  $[(\text{Me}_3\text{CCH}_2)_2\text{InCH}_2\text{PPh}_2]_2$ . The  $^{31}\text{P}$  and  $^1\text{H}$  spectra were also consistent with dimers. The  $^{31}\text{P}$  NMR spectral data revealed one concentration independent resonance at approximately -10 ppm for each compound,  $[\text{R}_2\text{MCH}_2\text{PPh}_2]_2$  ( $\text{M} = \text{Ga}$  or  $\text{In}$ ,  $\text{R} = \text{CH}_2\text{CMe}_3$  or  $\text{CH}_2\text{SiMe}_3$ ) (Table 5). Thus, there were no observable changes in the degree of association for any compound on the NMR time scale. The  $^1\text{H}$  NMR spectral data of the compounds  $[\text{R}_2\text{MCH}_2\text{PPh}_2]_2$  ( $\text{R} = \text{CH}_2\text{CMe}_3$ ,  $\text{CH}_2\text{SiMe}_3$ ) consisted of a doublet of doublets which was assigned to the methylene protons of the  $-\text{CH}_2\text{PPh}_2$  substituent, a singlet which was assigned to the  $-\text{CMe}_3$  of the  $-\text{CH}_2\text{YMe}_3$  ( $\text{Y} = \text{C}$  or  $\text{Si}$ ) substituent and a doublet which was assigned to the methylene protons of the  $-\text{CH}_2\text{YMe}_3$  ( $\text{Y} = \text{C}$  or  $\text{Si}$ ) substituent. The doublet ( $-\text{CH}_2\text{YMe}_3$ ) was upfield of the other resonances and appeared even farther upfield when the organic substituent was  $\text{CH}_2\text{SiMe}_3$  (-0.57 ppm for  $[(\text{Me}_3\text{SiCH}_2)_2\text{InCH}_2\text{PPh}_2]_2$  and -0.61 ppm for  $[(\text{Me}_3\text{SiCH}_2)_2\text{GaCH}_2\text{PPh}_2]_2$  as compared to 0.62 and 0.70 ppm for  $[(\text{Me}_3\text{CCH}_2)_2\text{GaCH}_2\text{PPh}_2]_2$  and  $[(\text{Me}_3\text{CCH}_2)_2\text{InCH}_2\text{PPh}_2]_2$ , respectively). The doublet of doublets appearing in the range 1.46 to 1.63 ppm was downfield of all the other resonances (except the phenyl protons) and was similar for all the  $[\text{R}_2\text{MCH}_2\text{PPh}_2]_2$  compounds.

In conclusion, it is noteworthy that the new compounds  $\text{R}_2\text{MCH}_2\text{PPh}_2$  ( $\text{R} = \text{CH}_2\text{CMe}_3$ ,  $\text{CH}_2\text{SiMe}_3$ ,  $\text{M} = \text{Ga}$ ,  $\text{In}$ ) are dimers in both the solid and solution phases, especially since these dimeric molecules can be viewed as simple adducts. In contrast, the related adducts  $(\text{Me}_3\text{CCH}_2)_3\text{Ga} \cdot \text{P}(\text{H})\text{Ph}_2^{20}$  and

$(\text{Me}_3\text{SiCH}_2)_3\text{Ga}\cdot\text{P}(\text{H})\text{Ph}_2$ <sup>20</sup> are significantly dissociated in benzene solution. The stability of the dimeric molecules  $(\text{R}_2\text{MCH}_2\text{PPh}_2)_2$  is further suggested by the observations that the gallium or indium moieties do not form stable room temperature adducts with  $\text{Et}_2\text{O}$ , THF, TMEDA or  $\text{NMe}_3$ . However, the compound  $(\text{Me}_3\text{SiCH}_2)_2\text{GaCH}_2\text{PPh}_2$  does form an apparent adduct with  $\text{NMe}_3$  when a four-fold excess of  $\text{NMe}_3$  is present in benzene solution. The stability of the dimers  $(\text{R}_2\text{MCH}_2\text{PPh}_2)_2$  in comparison to the simple adducts might be attributed to an increased Lewis acidity/basicity of the monomers. A more likely reason for the instability of adducts  $\text{R}_3\text{M}\cdot\text{P}(\text{H})\text{Ph}_2$  might be related to the greater solvation enthalpy of the free phosphine by the aromatic solvent benzene. Related solvation effects have been observed previously to be important for explaining the stabilities of other associated group 13-15 compound.<sup>21</sup>

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Supplementary Materials Available. Anisotropic thermal parameters (3 pp), a list of observed and calculated structure factor amplitudes (33 pp), and additional interatomic distances and angles (2 pp). For ordering information, see any current masthead page.

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Table 1. Experimental Data for the X-Ray Diffraction Study of  
 $[(\text{Me}_3\text{CCH}_2)_2\text{InCH}_2\text{PPh}_2]_2 \cdot \text{C}_6\text{D}_6$ .

(A) Unit Cell Parameters at 24 °C (297 K)

Crystal system: triclinic	Space group: $P\bar{1}$ ( $C_1^1$ ; No. 2)
$a = 13.142(3)\text{\AA}$	$v = 2639(1)\text{\AA}^3$
$b = 15.109(3)\text{\AA}$	Formula: $\text{C}_{46}\text{H}_{68}\text{In}_2\text{P}_2 \cdot \text{C}_6\text{D}_6$
$c = 15.746(4)\text{\AA}$	Formula wt: 912.5 + 84.1
$\alpha = 85.27(2)^\circ$	$Z = 2$
$\beta = 67.99(2)^\circ$	$D(\text{calcd}) = 1.25 \text{ g cm}^{-3}$
$\gamma = 66.00(1)^\circ$	

(B) Data Collection

Diffractometer: Syntex P2<sub>1</sub>

Radiation: Mo K $\alpha$  ( $\lambda = 0.710730\text{\AA}$ )

Monochromator: pyrolytic graphite in equatorial geometry ( $2\theta_m = 12.2^\circ$ , assumed to be 50% perfect/50% ideally mosaic for polarization correction).

Reflections measured:  $h, \pm k, \pm l$  for  $2\theta = 4.5\text{--}46.0^\circ$  ( $h = 0\text{--}14, k = -14\text{--}+16, l = -15\text{--}+16$ ); 7523 data were merged to 6532 independent reflections ( $R(I) = 1.5\%$  and  $R(WI) = 1.7\%$  for averaged pairs).

Scan type: coupled  $\theta(\text{crystal})\text{--}2\theta(\text{counter})$  scan at 4.0 deg/min in  $2\theta$  over the range  $[2\theta(\text{Mo K}\alpha_1) - 0.9]^\circ$  through  $[2\theta(\text{Mo K}\alpha_2) + 0.9]^\circ$ .

Background measurement: stationary crystal and counter at each extreme of the  $2\theta$ -scan; each for one-half total scan time.

Standard reflections: 3 (184, 238, 182) remeasured after each batch of 97 reflections; no significant fluctuations nor decay were observed.

Absorption corrections: data were corrected by interpolation in  $2\theta$  and  $\phi$  between the normalized transmission curves of  $\phi$ -scans of five close-to-axial reflections; their hkl indices,  $2\theta$ -values and maximum/minimum intensities are tabulated below:

234,	14.82°,	1.121
346,	18.25°,	1.132
358,	24.20°,	1.112
569,	27.57°,	1.136
689,	30.95°,	1.146.

Table 2. Final Atomic Coordinates for  $[(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2\text{CH}_2]_2 \cdot \text{C}_6\text{D}_6$ .

Atom	x	y	z
(A) Molecule 1			
In(1)	0.35666(4)	0.45045(3)	0.59834(3)
P(1)	0.36255(15)	0.55047(12)	0.44802(11)
C(1)	0.48850(54)	0.48017(50)	0.63865(43)
C(11)	0.16642(59)	0.52723(54)	0.69311(48)
C(12)	0.13583(60)	0.55221(53)	0.79511(46)
C(13)	0.19249(88)	0.45872(73)	0.83886(62)
C(14)	-0.00242(67)	0.59530(73)	0.84571(56)
C(15)	0.18186(86)	0.62719(72)	0.80527(67)
C(21)	0.42341(70)	0.30732(51)	0.52432(52)
C(22)	0.40467(75)	0.22415(53)	0.57808(53)
C(23)	0.47551(94)	0.12837(59)	0.51846(65)
C(24)	0.4618(10)	0.21201(68)	0.65589(66)
C(25)	0.2768(10)	0.24043(78)	0.62883(92)
C(31)	0.27461(59)	0.52447(43)	0.39378(44)
C(32)	0.14866(60)	0.56080(55)	0.44022(51)
C(33)	0.08008(71)	0.54056(64)	0.40181(65)
C(34)	0.13495(84)	0.48258(64)	0.31912(68)
C(35)	0.26091(84)	0.44609(59)	0.27270(61)
C(36)	0.33151(63)	0.46818(49)	0.31053(51)
C(41)	0.28656(54)	0.68266(44)	0.46909(45)
C(42)	0.25184(73)	0.73964(51)	0.40143(57)
C(43)	0.18780(90)	0.84292(61)	0.42361(77)
C(44)	0.16512(76)	0.88561(55)	0.50500(70)
C(45)	0.19954(77)	0.82773(58)	0.57105(61)
C(46)	0.25940(66)	0.72706(51)	0.55320(51)

(B) Molecule 2

In(2)	0.45212(4)	0.08503(3)	0.13516(3)
P(2)	0.42184(14)	0.14507(12)	-0.02359(11)
C(2)	0.46374(54)	-0.06707(45)	0.12540(45)
C(51)	0.28005(60)	0.18628(48)	0.24020(44)
C(52)	0.21030(60)	0.14622(47)	0.32557(43)
C(53)	0.10888(75)	0.23429(63)	0.39285(56)
C(54)	0.29582(83)	0.07843(69)	0.37340(57)
C(55)	0.15430(78)	0.08719(66)	0.29864(61)
C(61)	0.62513(70)	0.09709(66)	0.10007(54)
C(62)	0.65450(68)	0.13575(63)	0.16764(62)
C(63)	0.6540(16)	0.0569(18)	0.24374(93)
C(64)	0.78228(76)	0.12852(76)	0.13082(70)
C(65)	0.5680(11)	0.2269(11)	0.2196(15)
C(71)	0.27572(57)	0.16260(44)	-0.02610(46)
C(72)	0.20087(56)	0.12875(51)	0.04388(50)
C(73)	0.09222(64)	0.13934(54)	0.04175(55)
C(74)	0.05614(70)	0.18291(60)	-0.02935(59)
C(75)	0.13026(79)	0.21786(66)	-0.09694(61)
C(76)	0.24223(65)	0.20772(53)	-0.09669(49)
C(81)	0.42127(55)	0.26752(44)	-0.03896(42)
C(82)	0.51176(68)	0.28444(51)	-0.11062(53)
C(83)	0.51092(76)	0.37755(55)	-0.11738(59)
C(84)	0.42138(91)	0.45237(63)	-0.05395(67)
C(85)	0.32949(82)	0.43698(51)	0.01792(59)
C(86)	0.32869(67)	0.34412(49)	0.02508(50)

(C) C<sub>6</sub>D<sub>6</sub> of Solvation

C(91)	0.0301(10)	0.1232(12)	0.70457(81)
C(92)	-0.0274(15)	0.2277(12)	0.7169(12)
C(93)	-0.1275(12)	0.26962(94)	0.7886(11)
C(94)	-0.1750(10)	0.2140(11)	0.85214(86)
C(95)	-0.1157(12)	0.1141(10)	0.83778(87)
C(96)	-0.0184(11)	0.06800(93)	0.76751(88)



Table 3. Selected Interatomic Distances (Å) for  
 $[(\text{Me}_3\text{CCH}_2)_2\text{InCH}_2\text{PPh}_2]_2 \cdot \text{C}_6\text{D}_6$ .

<u>Molecule 1</u>		<u>Molecule 2</u>	
A) Indium-Ligand and P-CH <sub>2</sub> Distances			
In(1)-P(1)	2.694(2)	In(2)-P(2)	2.703(2)
In(1)-C(1)	2.261(8)	In(2)-C(2)	2.255(7)
In(1)-C(11)	2.226(8)	In(2)-C(51)	2.234(7)
In(1)-C(21)	2.216(7)	In(2)-C(61)	2.211(10)
*P(1)-C(1)	1.809(7)	*P(2)-C(2)	1.812(7)
B) Distances Involving the Neopentyl Ligands			
C(11)-C(12)	1.541(10)	C(51)-C(52)	1.551(10)
C(12)-C(13)	1.547(13)	C(52)-C(53)	1.550(11)
C(12)-C(14)	1.549(13)	C(52)-C(54)	1.565(13)
C(12)-C(15)	1.528(15)	C(52)-C(55)	1.532(14)
C(21)-C(22)	1.509(11)	C(61)-C(62)	1.489(13)
C(22)-C(23)	1.522(11)	C(62)-C(63)	1.619(22)
C(22)-C(24)	1.624(15)	C(62)-C(64)	1.516(15)
C(22)-C(25)	1.487(17)	C(62)-C(65)	1.439(20)
C) P-C Distances Within the PPh <sub>2</sub> Ligands			
P(1)-C(31)	1.839(8)	P(2)-C(71)	1.844(9)
P(1)-C(41)	1.826(6)	P(2)-C(81)	1.843(7)

\* This is the distance between the phosphorus in one asymmetric unit and the carbon in the adjacent unit.

Table 4. Selected Interatomic Angles (deg) for  $[(\text{Me}_3\text{CCH}_2)_2\text{InCH}_2\text{PPh}_2]_2 \cdot \text{C}_6\text{D}_6$ .

<u>Molecule 1</u>		<u>Molecule 2</u>	
A) Angles Involving the Core Atoms of the Dimer			
P(1)-In(1)-C(1)	100.76(19)	P(2)-In(2)-C(2)	99.35(18)
P(1)-In(1)-C(11)	102.06(21)	P(2)-In(2)-C(51)	101.94(19)
P(1)-In(1)-C(21)	94.85(22)	P(2)-In(2)-C(61)	96.49(24)
*P(1)-C(1)-In(1)	116.94(35)	*P(2)-C(2)-In(2)	114.60(24)
C(1)-In(1)-C(11)	113.57(27)	C(2)-In(2)-C(51)	113.57(26)
C(1)-In(1)-C(21)	116.81(28)	C(2)-In(2)-C(61)	115.69(30)
C(11)-In(1)-C(21)	122.13(30)	C(51)-In(2)-C(61)	123.10(31)
*C(1)-P(1)-In(1)	114.42(24)	*C(2)-P(2)-In(2)	116.86(35)
B) Selected Angles Involving the Neopentyl Ligands			
In(1)-C(11)-C(12)	120.42(52)	In(2)-C(51)-C(52)	120.07(48)
In(1)-C(21)-C(22)	119.35(57)	In(2)-C(61)-C(62)	122.76(64)
C) Angles Involving the Phosphide Ligands			
In(1)-P(1)-C(31)	108.66(23)	In(2)-P(2)-C(71)	114.90(24)
In(1)-P(1)-C(41)	115.92(23)	In(2)-P(2)-C(81)	109.06(23)
*C(1)-P(1)-C(31)	106.92(33)	*C(2)-P(2)-C(71)	106.58(33)
*C(1)-P(1)-C(41)	108.31(31)	*C(2)-P(2)-C(81)	107.81(32)
C(31)-P(1)-C(41)	101.48(32)	C(71)-P(2)-C(81)	103.08(32)
P(1)-C(31)-C(32)	118.25(55)	P(2)-C(71)-C(72)	119.08(55)
P(1)-C(31)-C(36)	120.57(56)	P(2)-C(71)-C(76)	120.04(57)
P(1)-C(41)-C(42)	120.18(57)	P(2)-C(81)-C(82)	121.64(55)
P(1)-C(41)-C(46)	120.05(56)	P(2)-C(81)-C(86)	118.32(54)

\* This is the angle made by atoms in one asymmetric unit with atoms in the adjacent unit.

Table 5.  $^1\text{H}$  NMR and  $^{31}\text{P}$  NMR Spectral Data for  $\text{R}_2\text{MCH}_2\text{PPh}_2$  ( $\text{R} = \text{CH}_2\text{CMe}_3$  or  $\text{CH}_2\text{SiMe}_3$ ;  $\text{M} = \text{Ga}$  or  $\text{In}$ )

## Compounds.

	$\delta\text{-PCH}_2 - (^2\text{J}(\text{PCH})/^3\text{J}(\text{PMCH}))$	$\delta\text{-CMe}_3^-$	$\delta\text{-CCH}_2^-$	$^{31}\text{P}(\text{H})$
		$\delta\text{-SiMe}_3^-$	$\delta\text{-SiCH}_2 - (^3\text{J}(\text{PMCH}))$	
$[\text{Np}_2\text{GaCH}_2\text{PPh}_2]_2$	1.63 dd (11.7/8.1)	1.03 s	+0.62 d (3.6)	-10.1
$[\text{Np}_2\text{InCH}_2\text{PPh}_2]_2$	1.46 dd ( 9.9/4.5)	0.90 s	+0.70 d (8.6)	- 8.4
$[\text{R}_2\text{GaCH}_2\text{PPh}_2]_2$	1.59 dd (10.8/7.2)	0.11 s	-0.61 d (4.2)	-10.2
$[\text{R}_2\text{InCH}_2\text{PPh}_2]_2$	1.50 dd (10.8/4.5)	0.14 s	-0.57 d (3.6)	-10.0

 $\text{R} = \text{CH}_2\text{SiMe}_3$  $\text{Np} = \text{CH}_2\text{CMe}_3$

CAPTIONS TO FIGURES

Figure 1. Labeling of atoms for molecule 1 of  $[(\text{Me}_3\text{CCH}_2)_2\text{InCH}_2\text{PPh}_2]_2$ . The P-In-C-P-In-C system has been stippled so as to show clearly its "chair" conformation. Atoms of the basic asymmetric unit have normal labels; those in the other half of the molecule (related to the basic unit by the transformation  $1-x, 1-y, 1-z$ ) are labeled with a prime. All hydrogen atoms are omitted. [ORTEP diagram; 30% probability ellipsoids.]

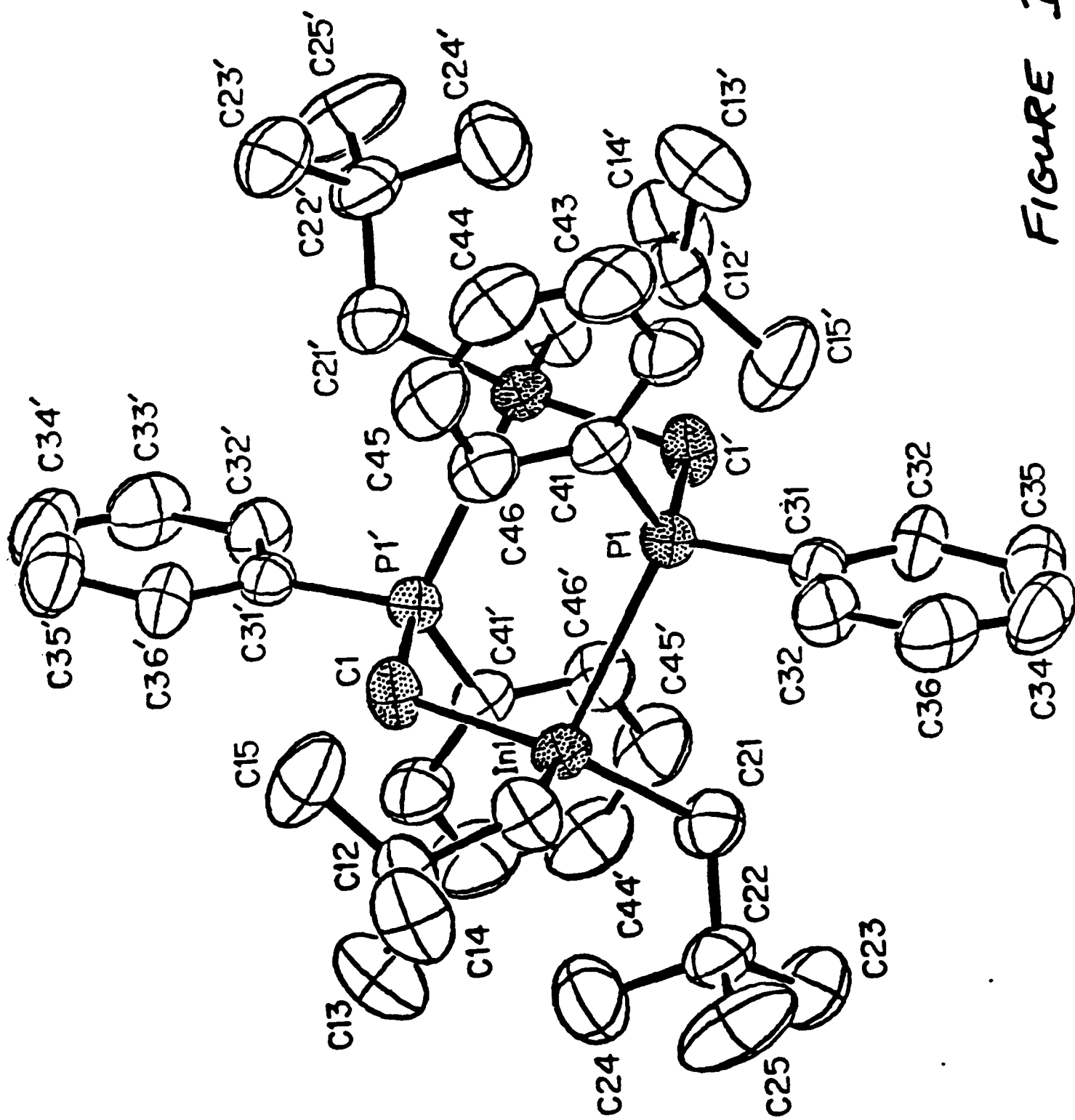


FIGURE 1

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Chemistry Division, Code 1113  
800 North Quincy Street  
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Port Hueneme, CA 93043

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